STOCHASTIC MODELING OF PETROLEUM RESID - THE USE OF REACTIVITY INFORMATION IN STRUCTURE DETERMINATION

Achin Vasudeva, Ankush Kumar
Department of Chemical Engineering
University of Delaware, Newark, DE 19716

Michael T. Klein
College of Engineering
Rutgers, The State University of New Jersey
Piscataway, New Jersey 08854-8058

INTRODUCTION

Structural characterization of petroleum resid has gained importance in the petroleum industry in recent years owing to the increasing abundance of such material in the petroleum produced worldwide. It is estimated that at least 85% of the world proven reserves of petroleum contain large amounts of "heavy" material boiling above 650°F. On the other hand, according to recent reports, about 50% of the petroleum products consumed in the United States at the present time are gasoline and an additional 40% are other distillate fuels boiling below about 650°F [1]. These trends have focused attention on the efficient upgrading of petroleum resids to light distillates. In order to meet the challenge of optimal upgrading of heavy petroleum fractions, a detailed understanding of the resid structure is required.

The traditional approach for modeling such complex systems has been to use lumped models where molecular species are grouped according to some physical property, such as boiling point or solubility [2]. However, lumped models are clearly incapable of providing molecular information about the feedstock since, by lumping molecules according to some physical characteristic, the molecular detail is lost. With recent government regulations having established concentration limits for specific molecules in a feedstock, an example being benzene, a known carcinogen, molecularly explicit models are required that can predict the concentrations of individual species. Lumping strategies can also lead to difficulties in developing an accurate model. For instance, a C_{10} paraffin and a C_{10} aromatic (alkyl benzene) would be lumped together in the same boiling point range and the lumped model would represent them by the same pseudo component. Clearly, however, an alkyl benzene would react quite differently from a paraffin.

The limitations of lumped models motivate the development of molecule-based models. The development of such molecularly explicit models has been made possible by the explosion in available computational resources. To develop molecule-based models, the initial conditions need to incorporate molecular level details. For models dealing with a feedstock as complex as a petroleum resid, which has tens of thousands of molecules, tracking each species is impractical considering the prohibitively large solution times associated with solving such a reaction model. A stochastic description of the complex feedstock provides a path forward. Such a model retains the molecular detail of the feedstock and at the same time can be reduced to generate a small set of representative molecules (of the order of ~ 50-100) to be used in the reaction model.

STOCHASTIC DESCRIPTION OF PETROLEUM RESID

The construction algorithm for petroleum resid is presented in Figure 1. For each molecule, the molecular type (e.g., paraffin, naphthenic, aromatic/resin, or asphaltene) is determined first. The stochastic description of a feedstock involves viewing each molecule as a collection of molecular attributes. Once the molecular type has been identified, the value of each attribute needed to specify the molecule is determined. For instance, an aromatic molecule would be specified by the number of aromatic rings, the number of naphthenic and thiophenic rings attached to it, the number of side chains, the length of side chains and the number of side chain sulfur atoms.
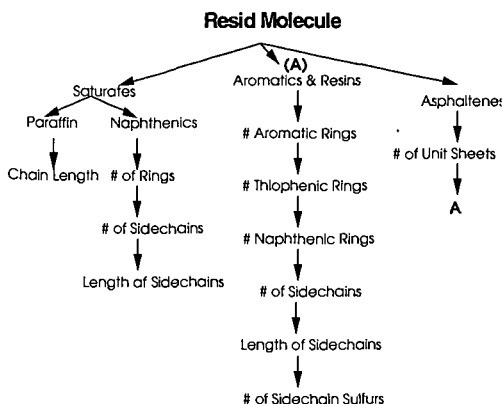
Resid Molecule

Fig. 1   Construction algorithm for petroleum resid

Each molecular attribute is characterized by a probability distribution function (pdf) which provides the quantitative probability of finding the value or less of a given attribute. The applicability of probability distribution functions to describe complex mixtures in general and petroleum fractions in particular has been well documented in the literature [7,9,11,14,17]. Monte Carlo sampling of the set of pdf's (one set for each feed) provides a large ensemble of molecules (of the order of 10^5). The properties of this set of molecules generated are compared to experimentally obtained analytical data to obtain an optimal set of pdf parameters, which define the feedstock. The pdf parameters are optimized using the following objective function:

$$\chi^2 = \left(\frac{MW_{exp} - MW_{pred}}{0.05 * MW_{exp}}\right)^2 + \left(\frac{HtoC_{exp} - HtoC_{pred}}{0.02 * HtoC_{pred}}\right)^2 +$$
$$+ \left(\frac{Halpha_{exp} - Halpha_{pred}}{0.02}\right)^2 + \left(\frac{Harom_{exp} - Harom_{pred}}{0.01}\right)^2$$
$$+ \left(\frac{1}{\#Comps}\right) \sum_{i=1}^{\#Comps} \left(\frac{SARAWt_{i,exp} + SARAWt_{i,pred}}{0.03}\right)^2$$
$$+ \left(\frac{1}{\#Fracs}\right) \sum_{i=1}^{\#Fracs} \left(\frac{SIMDIS_{i,exp} - SIMDIS_{i,pred}}{0.01}\right)^2 \tag{1}$$

The numerator in each term of the above equation is the difference between the experimentally determined property and the predicted property, and the denominator is a weighting factor equal to one experimental standard deviation. A simulated annealing global optimization technique is employed to minimize the objective function and generate an optimal set of pdf parameters.

In general, the only information available about petroleum resids are some average properties like molecular weight (Vapor Pressure Osmometry), elemental analysis, boiling point distribution (SIMDIS) and NMR (^{1}H and ^{13}C) data. Analytical techniques like GC/MS which yield molecular level details also provide only broad lumps due to the extreme complexity of the feedstock. This limited amount of structural information often renders the optimal set of pdf parameters non-unique, thus preventing the development of an accurate stochastic description of the resid. To tackle the issue of non-uniqueness, further structural information is required. One possible source of such information is a detailed product distribution from the controlled reaction of the resid.

The approach adopted in this study has been to crack the resid in the presence of hydrogen under conditions where the reaction pathways and associated rate constants can be estimated with reasonable accuracy. The light fractions obtained as a result of the controlled reaction are subject to detailed compositional analyses (GC/MS, High Detail Hydrocarbon Analysis) to obtain a molecularly explicit description of the product. This information is incorporated into the objective function as a term representing the difference between experimental and predicted weight fractions of all the species in the product. The objective function is thus modified as follows:

$$\chi^2 = \left(\frac{MW_{exp} - MW_{pred}}{0.05 * MW_{exp}}\right)^2 + \left(\frac{HtoC_{exp} - HtoC_{pred}}{0.02 * HtoC_{pred}}\right)^2 +$$

$$+ \left(\frac{Halpha_{exp} - Halpha_{pred}}{0.02}\right)^2 + \left(\frac{Harom_{exp} - Harom_{pred}}{0.01}\right)^2$$

$$+ \left(\frac{1}{\#Comps}\right) \sum_{i=1}^{\#Comps} \left(\frac{SARAWt_{i,exp} + SARAWt_{i,pred}}{0.03}\right)^2$$

$$+ \left(\frac{1}{\#Fracs}\right) \sum_{i=1}^{\#Fracs} \left(\frac{SIMDIS_{i,exp} - SIMDIS_{i,pred}}{0.01}\right)^2$$

$$+ \left(\frac{1}{\#Species}\right) \sum_{i=0}^{T} \sum_{i=1}^{\#Species} \left(\frac{Wtfrac_{i,exp} - Wtfrac_{i,pred}}{0.01}\right)^2$$

(2)

Minimization of the modified objective function thus yields an improved stochastic description of the feedstock.

In cases where such complex feedstocks are to be part of a molecularly explicit reaction model, a much more compact molecular description of the feedstock is desirable. This is because handling the thousands of molecules generated by Monte Carlo sampling and their associated reactions and rate constants can result in enormous solution times using present day computers. This molecular lumping is achieved by means of a quadrature technique, wherein ordered sampling of attribute values based on equiprobable regions (to allow sampling over the entire range of attribute values) results in the finite set of representative molecules (of the order of ~10-100 molecules) to be used in the reaction model. The entire modeling approach is thus outlined in Fig.2.
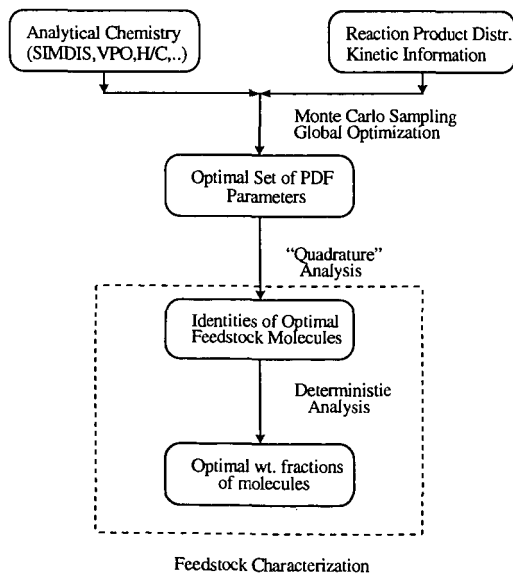

Feedstock Characterization

Fig. 2. Modeling approach for stochastic description of petroleum resid

EXPERIMENTAL

The resid was cracked in the presence of excess hydrogen in a flow reactor setup. The catalyst precursor employed was molybdenum naphthenate containing 6% by wt. Mo (obtained from The Shephard Oil Company). Molybdenum naphthenate was sulfided in situ by sulfur present in the petroleum resid to generate the active catalytic species, MoS_2. The particular choice of dispersed catalyst ensured sufficient conversion of resid to light products while at the same time inhibiting coke production [6,8,15]. A catalyst concentration of 3000 ppm (by weight of Mo in resid) was used. The resid was dissolved in toluene in the ratio of 1:3.5 by weight (resid : toluene). Toluene was the choice of solvent because of its excellent solvation properties (for the resid under investigation) and its inertness under reaction conditions. The hydrogen pressure in the reactor was maintained at 1100 psig and the reaction was carried out at 470°C. The liquid flow rate was about 0.28 ml/min while the hydrogen flow rate was controlled at 150 std ml/min. The residence time of the liquid in the reactor was about 15 minutes.

The gas product was analyzed online in an HP 5890 GC equipped with a 100 m HP-1 capillary column (ID : 0.25 mm, film thickness : 0.5 μm) coupled with an FID for identification of hydrocarbons and a 1 m HayeSep C packed column coupled with a TCD for detection of polar gases such as ammonia and hydrogen sulfide. The liquid product was collected and subjected to HDHA (High Detail Hydrocarbon Analysis) and GC/MS analysis to yield the product distribution.

REACTION MODEL

The driving force for cracking of petroleum resid in the presence of excess hydrogen employing molybdenum naphthenate as the catalyst precursor is thermal activation. At a mechanistic level, the catalyst has no effect on C-C bond cracking so that the initial population of free radicals is determined by the severity of conditions. The next step in the reaction sequence is the saturation of the reactive fragments, which is promoted by the catalyst. The efficient uptake of hydrogen facilitated by the catalyst ensures that the reactive fragments do not undergo fast undesirable reactions, such as condensation reactions, which give rise to the appearance of mesophase and then to coke deposition. Instead, the catalyst controls the rate of free radical propagation that, via β-scission reaction, favors the process of resid conversion to lighter products [4,5].

A pathways level model describing the resid cracking reaction has been employed in this study. At the pathways level, the main reactions are considered to be breaking of intersheet linkages for asphaltene molecules and side chain cracking reactions including dealkylation for aromatic and naphthenic molecules. Hydrogenation of ring molecules and subsequent ring opening, although not significant, are also considered. The above reactions are used to generate a reaction network consisting of about 250 molecular species. The rate constants for all the species and their associated reactions have been estimated from previous studies conducted with model compounds under similar reaction conditions [12,13]. For example, rate constants for alkyl aromatics undergoing side chain cracking are calculated from the reaction of pentadecyl benzene (PDB) using first order approximations as :

$$k_i = k_{PDB} (i/15)^{0.5} \tag{3}$$

where i is the number of carbon atoms in the side chain of the alkyl aromatic molecule. The breaking of intersheet linkages in asphaltene molecules has also been modeled as side chain cracking of alkyl aromatic species. Similarly, the rate constants for reactions of alkyl hydroaromatic and alkyl naphthenic species have been estimated from available data on ethyl tetralin and tridecyl cyclohexane respectively.

Monte Carlo sampling of the pdf parameters describing the structural attributes of resid molecules generates a large ensemble of molecules which provide the initial condition for the reaction model. Solution of the reaction model results in predicted product concentrations which are compared to experimentally obtained data and the difference forms part of the objective function, which is minimized. Reactivity information is thus utilized to develop an improved stochastic description of the petroleum resid.

REFERENCES

1. Altgelt, K. H., and Boduszynski, M. M., *Composition and Analysis of Heavy Petroleum Fractions*, Marcel Dekker Inc., New York, pp 1-7 (1994).
2. Beaton, W. I., and Bertolacini, R. J., *Catalysis Reviews - Science and Engineering*, 33, 281-317 (1991).
3. Campbell, D. M., *Stochastic Modeling of Structure and Reaction in Hydrocarbon Conversion*, Ph.D. Dissertation, University of Delaware (1998).
4. Cebolla, V. L., Membrado, L., Vela, J., Bacaud, R., and Rouleau, L., *Energy & Fuels*, 9, 901-905 (1995).
5. Del Bianco, A., Panarati, N., Di Carlo, S., Beltrame, P. L., and Carniti, P., *Energy & Fuels*, 8, 593-597 (1994).
6. Fixari, B., Peureux, S., Elmouchnino, J., Le Perchec, P., Vrinat, M., and Morel, F., *Energy & Fuels*, 8, 588-592 (1994).
7. Flory, P. J., *J. Am. Chem. Soc.*, 58, 1877 (1936).
8. Kim, H., and Curtis, C. W., *Energy & Fuels*, 4, 206-214 (1990).
9. Libanati, C., Monte Carlo Simulation of Complex Reactive Macromolecular Systems, Ph.D. Dissertation, University of Delaware (1992).
10. Logwinuk, A. K., and Caldwell, D. L., *Chem. Econ. Eng. Rev.*, 15, 31 (1983).
11. Pederson, K. S., Blilie, A. L., and Meisingset, K. K., *Ind. Eng. Chem. Res.*, 31, 1378-1384 (1992).
12. Savage, P. E., *Chemical and Mathematical Modeling of Asphaltene Reaction Pathways*, Ph.D. Dissertation, University of Delaware (1986).
13. Savage, P. E., and Klein, M.T., *Ind. Eng. Chem. Res.*, 26, 488-494 (1987).
14. Shibata, S. K., Sandler, S. I., and Behrens, R. A., *Chem. Eng. Sci.*, 42, 1977-1988 (1987).
15. Ting, P., Curtis, C. W., and Cronauer, D. C., *Energy & Fuels*, 6, 511-518 (1992).
16. Trauth, D. M., *Structure of Complex Mixtures through Characterization, Reaction, and Modeling*, Ph.D. Dissertation, University of Delaware (1990).
17. Whitson, C. H., *Soc. Pet. Eng. J.*, 683 (1990).